

# **FINAL REPORT**

## **NANOCATALYSIS AND NANOSTRUCTURES: ATOMIC - SCALE DESIGN OF CHEMICAL AND SENSING ACTIVITY**

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**Prepared by:**

**Uzi Landman**

**School of physics**

**Georgia Institute of Technology**

**Atlanta, GA 30332-0430**

**Uzi. [Landman@physics.gatech.edu](mailto:Landman@physics.gatech.edu)**

**AFOSR Contact: Dr. Michal Berman**

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## I. Abstract / Summary

(a) Control and tunability of the catalytic oxidation of CO by gold clusters deposited on MgO surfaces grown on molybdenum, Mo(100), to various thicknesses, were explored through temperature programmed reaction measurements on mass selected 20-atom gold clusters and via first-principles density-functional theory calculations. Au<sub>20</sub> was chosen since in the gas phase it is characterized as an extraordinary stable tetrahedral pyramidal structure. Dependencies of the catalytic activities and microscopic reaction mechanisms on the thickness and stoichiometry of the MgO films, and on the dimensionalities and structures of the adsorbed gold clusters were demonstrated and elucidated. Langmuir-Hinshelwood mechanisms and reaction barriers corresponding to observed low and high temperature CO oxidation reactions were calculated and analyzed. These reactions involve adsorbed O<sub>2</sub> molecules, which are activated to a superoxo- or peroxo-like state through partial occupation of the antibonding orbitals. In some cases we find activated, dissociative adsorption of oxygen molecules, adsorbing at the cluster peripheral interface with the MgO surface. The reactant CO molecules adsorb either on the MgO surface in the cluster proximity, or bind directly to the gold cluster. Along with the oxidation reactions on stoichiometric ultra thin MgO films we also studied reactions catalyzed by Au<sub>20</sub> nanoclusters adsorbed on relatively thick defect-poor MgO films supported on Mo, and on defect-rich thick MgO surfaces containing oxygen vacancy defects.

(b) Aiming at exploring novel methods for control of Nanocatalytic activity we have investigated the use of external electric fields as a way for switching the chemical activity in a nanocatalytic systems, and have studied the interaction of oxygen with gold

nanowires. With the use of first-principles quantum mechanical calculations that include an externally applied electric potential, we have shown that the structure, dimensionality, and properties (including chemical reactivity) of gold nanoclusters (containing up to 20 atoms) deposited on (non-defective) thin films of MgO which themselves are supported on a Mo(100) substrate, can be controlled and modified by electric fields applied across the catalytic nanostructure. This electric-field-induced effect originates from excess electronic charge that transfers from the underlying substrate across the metal-oxide, and accumulates at the Au cluster interface with the MgO film.

In our quantum simulation of suspended oxygenated Au nanowires we have explored molecular and dissociative modes of oxygen incorporation, and via first principles electronic structure calculations, coupled with non-equilibrium Greens function electric transport calculations, we have predicted enhanced strength of the Au nanowires by molecular oxygen adsorption, a metal-insulator transition that set in beyond a certain degree of elongation in oxygen containing Au nanowires, and the development of local magnetic moments in Au nanowires with incorporated atomic oxygen.

## II. Archival Publications

1. "Charging Effects on Bonding and catalyzed oxidation of CO on Au<sub>8</sub> Clusters Supported on MgO", B. Yoon, H. Hakkinen, U. Landman, A. Wörz, S. Abbet, K. Judai, U. Heiz, *Science*, 307, 403 (2005).
2. "Materials by Numbers: Computations as Tools of Discovery", U. Landman, perspective article in *Proc. Nat. Acad. Sci. (USA)*, 102, 6671 (2005).
3. "Water Enhanced Catalysis of CO oxidation on Free and Supported Gold Nanoclusters", A. Bongiorno and U. Landman, *Phys. Rev. Lett.* 95, 106102 (2005).



4. "Oxidation of Small Gas Phase Pd Clusters: A Density Functional Study", B. Huber, H. Hakkinen, U. Landman, M. Moseler, *Comput. Mater. Sci.* 35, 371-374 (2006).
5. "Bonding Trends and Dimensionality Crossover of Gold Nanoclusters on Metal-supported MgO Thin Films", D. Ricci, A. Bongiorno, G. Pacchioni, U. Landman, *Phys. Rev. Lett.* 97, 36106 (2006).
6. "Low temperature gold catalysis", M. Arenz, U. Landman, U. Heiz, *Chem. Phys. Phys. Chem.*, 7, 1871 (2006).
7. "Structural Evolution of Au Nanoclusters: From Planar to cage to nanotube Motifs", X. Xing, B. Yoon, J. H. Parks, U. Landman, *Phys. Rev. B* 74, 165423 (2006).
8. "size-dependent evolution of structures and chemical reactivity of gold nanoclusters: Au<sub>N</sub><sup>-</sup>, N=15-24", B. Yoon, P. Koshkinen, B. Huber, O. Kostki, B. von Issendorff, H. Hakkinen, M. Moseler, U. Landman, *Chem. Phys. Phys. Chem.* 8, 157 (2007).
9. "Predicted Oxidation of CO Catalyzed by Au Nanoclusters on a Thin Defect-Free MgO Film Supported on a Mo(100) Surface", C. Zhang, B. Yoon, and U. Landman, *J. Am. Chem. Soc (Communication)* 129, 2229 (2007).
10. "Factors in gold nanocatalysis: oxidation of CO in the non-scalable size regime", M. Arenz, U. Landman, U. Heiz, *Topics in Catalysis* 44, 145 (2007).
11. "Electric Field Control of Structure, Dimensionality and Reactivity of Gold Nanoclusters on Metal-Supported MgO Films", B. Yoon and U. Landman, *Phys. Rev. Lett.* 100, 056102 (2008).
12. "Bonding, conductance, and magnetization of oxygenate Au nanowires", C. Zhang and U. Landman, *Phys. Rev. Lett.* 100, 046801 (2008).
13. "Control and manipulation of Au nanocatalysis: effects of metal oxide support thickness and composition", Chris Harding, Vahideh Habibpour, Sebastian Kunz, Adrian Nam-Su Farnbacher, Ueli Heiz, Bokwon Yoon, and Uzi Landman, *J Am. Chem. Soc.* January (2009).

## BOOK

"Nanocatalysis", U. Heiz and U. Landman, Hard Cover (2006); Paperback Edition (2007) (Springer, Heidelberg. New York).

## III. Researchers Supported by the Grant

1. Dr. Uzi Landman, Professor and Principal Investigator.

2. Dr. Bokwon Yoon Research Scientist II.
3. Dr. Robert Barnett, Senior Research Scientist
4. Dr. Chun Zhang, Post doctoral fellow
5. Dr. Hannu Hakkinen, Senior Research scientist
6. Dr. David Ricci, Post doctoral fellow
7. Dr. Angelo Bongiorno, Post doctoral fellow

#### **IV. Control and manipulation of Au nanocatalysis: effects of metal oxide support thickness and composition**

This section contains along with the results of theoretical calculations performed at the Center for Computational Materials Science at Georgia Tech, experimental results obtained in the group of Professor Ueli Heiz at the Technical University of Munich. The material in this section is the basis for paper no. 13 in the list of publication (part II of this report).

The introductory section contains a summary of our research in nanocatalysis for the duration of this grant.

## Introduction

One of the principal goals of modern research in chemical catalysis is the development of methods for further control and manipulation of the activity, selectivity, and specificity of catalytic systems.<sup>1,2</sup> This can be achieved in various ways, including: (i) selection of the catalyst material and composition; (ii) manipulations of the atomic structure, morphology and shape of the catalyst; (iii) choice of the support (composition, structure, thickness<sup>3,4</sup>) and (iv) the use of externally applied electric or electromagnetic fields.<sup>5</sup> Particle size plays an important role in determining the chemical reactivity of material aggregates. A main endeavor in current catalytic research aims at characterizing, understanding, controlling, and utilizing the effects of particle size on catalytic properties. With this in mind, each of the aforementioned ways of controlling and modifying catalytic activity may be explored also in conjunction with variations of the size of the catalytic particles under investigation. Indeed, numerous studies have demonstrated, for a broad range of size scales, dependencies of, and correlations between the catalytic properties and the size or dimensionality of the catalytic material. For example, it has been shown<sup>6</sup> that for a number of reactions the catalytic activity of single crystal surfaces can be modified by using metal nanoparticles with an average size down to a few nanometers. In this size range it was found that nanocrystallites of different size may exhibit different structural motifs characterized by different proportions of exposed crystallographic facets (with corresponding different chemical reactivities), thus resulting in size-dependent variations of the catalytic activity of the nanocrystallites.<sup>6-8</sup>

Moreover, new catalytic properties emerge, which could not have been anticipated through extrapolation of behavior known for larger sizes, when the reduction of the size of metal catalyst particles reaches the ultimate nanocluster regime, that is clusters comprised of about ten to up to twenty atoms ( $\leq 1$  nm in “diameter”). In this size range the nanocluster may be viewed as a quasi “zero dimensional”, 0D, quantum dot whose physical and chemical properties are dominantly affected by quantum size effects<sup>1, 2, 9-14</sup> originating from electrons trapped in a region of finite size (in all three dimensions), including coupling to the supporting surface. As aforementioned, in this regime, which is the one where gold clusters exhibit unique reactivities (see refs<sup>10, 13, 14</sup> and discussion below), extrapolations from larger sizes as using arguments relying on surface to volume ratios and scaling relations based on enumeration of special sites (e.g. corner atoms) as a function of size<sup>15-17</sup> are not operative; indeed, in this size scale almost all the atoms of the metal cluster are essentially surface atoms, and almost all can be classified as under-coordinated (compared to bulk). Instead, in this important regime, which is the focus of our research in this paper, one must resort to quantum mechanical calculations that highlight the correlations between the electronic structure of the coupled cluster-substrate catalytic system (namely positioning of energy levels, particularly the electrons of the gold cluster belonging to the *sd* manifold with energies in the vicinity of the top of the occupied spectral range) and the geometrical arrangement of the atoms (including their distortions in the course of reactions, which we termed as “dynamical fluctuonality”<sup>18</sup>) on an atom-by-atom level – that is, when every atom counts, and where “small is different” in an essential, i.e. non-scalable, manner. This is indeed the approach that we have taken in earlier studies<sup>1, 2, 4, 5, 13, 14, 18</sup> and the one that we use in this study.



While the utilization of reactive metals, e.g. transition metals, as well as some coinage metals (like silver, palladium and platinum), in catalytic processes is rather common, the catalytic properties of gold are less known and they remain largely unexploited; indeed, till about two decades ago, gold has been considered to be strictly inert. While this is the case for bulk gold, when prepared as aggregates (clusters) of nanometer dimensions gold exhibits interesting, potent and promising catalytic activity with unique specificity and selectivity characteristics.<sup>1, 2, 13, 18-20</sup> In particular, joint experiments and theoretical investigations of the catalytic oxidation of CO on size-selected gold clusters supported on relatively thick, defect (F-center) rich, MgO surfaces have shown low-temperature catalytic combustion to occur at temperatures as low as 140 K for Au<sub>n</sub> clusters with  $8 \leq n \leq 20$  gold atoms, that is, a non-planar (two-layer) Au<sub>8</sub> nanocluster emerged as the smallest one to exhibit catalytic activity.<sup>13</sup>

We wish to reemphasize here that the emergence<sup>13</sup> of such sub-nanometer scale bilayer gold clusters (starting with the gold octamer), supported on thick metal-oxide (MgO) surfaces containing oxygen vacancies (F-centers), as the ones exhibiting catalytic activity, has its origins in two main factors: (i) the quantum size-effect where the confinement of the electrons (defined by the adsorbed cluster structure and dimensionality, and including the charging effect from the surface defects) serves to determine the positioning of the chemically active energy levels (the sd orbitals of gold lying near the Fermi level), and (ii) the cluster proximity effect, where the distances between the adsorbed reactant molecules is restricted by the nanometer (or subnanometer) size of the cluster, thus lowering (concomitantly with the optimal positioning of energy

levels noted above, and charging induced activation) the enthalpic and entropic reaction activation barriers.

It is pertinent to remark here that most recent aberration-corrected transmission electron microscopy investigations<sup>21</sup> used for identification of the active catalytic gold species among the many present on real catalysts, have found that the high catalytic activity for carbon monoxide oxidation is unambiguously correlated with the presence of bilayer clusters (supported on a metal-oxide) that are less than 1 nm in diameter and contain on the order of only 10 gold atoms. Interestingly, these studies, which are fully consistent with the early theoretical and experimental investigations described above<sup>13, 14, 18</sup>, found that the catalytically active subnanometer gold bilayer clusters represented only  $1.05 \pm 0.72$  % of the total Au loading, with the remaining  $98.82 \pm 0.8$  atomic % of Au being larger particles. The authors further emphasized their findings by stating that “The observation that the active species in our Au/FeO<sub>x</sub> catalysts consist of subnanometer clusters differs from numerous earlier investigations that identified 2- to 5-nm particles as the critical nanostructures”. The authors also remarked about experimental difficulties in detecting these subnanometer clusters, stating that “... it is probable that these minority Au species would not be easily detected with traditional ‘bulk’ techniques such as extended x-ray absorption fine structure or Mossbauer spectroscopy, or even by surface analysis techniques such as x-ray photoelectron spectroscopy (XPS), because their contribution to the total signal would be minimal compared with that of the larger nanoparticles”.

In the earlier theoretical investigations<sup>13, 14, 18</sup> charging of the adsorbed metal cluster through partial electron transfer from the oxygen vacancy F-centre (FC) defects

(or other Lewis basic defect sites) was found to play a key role in anchoring the gold cluster to the metal-oxide (MgO) surface (thus enhancing stability of the adsorbed gold nanoclusters against coalescence and sintering), and in activation and promotion of the reactant molecules. The change of the charge state of the cluster (through charge transfer from the underlying substrate, causing an upward shift of the cluster energy levels and enhanced population near the Fermi level) and consequent occupation of the antibonding  $2\pi^*$  orbital of  $O_2$  (which, upon adsorption of the oxygen molecule on the cluster, drops below the Fermi level,  $E_F$ , of the supported gold nanocluster, and mixes with the sd states near  $E_F$ ) leads to activation of the O-O bond and have been identified as underlying the catalytic activity.<sup>2, 10, 13, 14, 18</sup> The unusual activation of oxygen upon adsorption is portrayed in elongation of  $d(O-O)$  to about 1.35 Å, corresponding to a superoxo-like state, or to  $d(O-O) > 1.4$  Å, corresponding to a peroxo-like state. Interestingly, in most oxidation (combustion) reactions catalyzed by gold nanoclusters, the oxygen molecule is activated through its interaction with the gold nanocluster, but does not dissociate, whereas for reactions catalyzed on extended metal surfaces dissociation of the adsorbed oxygen molecules is the common route to oxidation reactions.

Another key factor that influences the catalytic activity of gold nanoclusters is their ability to distort in the course of interaction with the reactants. This property has been termed “dynamical fluctuonality” and it is unique to clusters in the nanometer size range.<sup>18</sup> Such structural fluxional distortions enable adsorption and activation of the reactants, as well as lower the activation barriers of reactions between the adsorbed reactants.

Recently it has been predicted theoretically <sup>3, 4</sup> and confirmed experimentally <sup>22</sup> that a dimensionality crossover will occur for gold clusters deposited on thin metal oxide films grown on appropriate metal surfaces (e.g. MgO grown on Mo(100) or Ag(100)) as a function of the metal-oxide film thickness. Thinner MgO films with less than 7-8 layers favoring two-dimensional wetting gold island structures, whereas on thicker films the dimensionality of the free clusters are maintained. The stabilization has been shown to be caused by the accumulation of excess electronic charge, originating from the underlying metal, at the cluster interface with the MgO film. This has been predicted <sup>4</sup> to result in catalytic activity of gold nanoclusters adsorbed on thin MgO films, even when the films have no Lewis basic defect sites (e.g. F-centers), provided that the films are thin enough.

The experimental and theoretical investigations presented herein aim at demonstrating the effect of metal-oxide film thickness on the catalytic activity and reaction mechanisms of adsorbed gold nanoclusters (in particular Au<sub>20</sub>). We indeed show that sufficiently thin MgO films can serve as supports in gold nanocatalysis, even when they do not contain Lewis basic defect sites, and identify low and high temperature reaction channels. We also contrast these results with catalytic CO oxidation on thick, defect-rich MgO films. Conceptually we show the active site on the cluster to be characterized by enhanced electron density, which activates or dissociates the adsorbed oxygen molecule and promotes the bonding of CO. The location of the enhanced charge density is shown to sensitively depend on the characteristics of the underlying metal oxide.



## Methods

(a) *Experimental methods.* The model catalytic systems used in these investigations consist of Au<sub>20</sub> clusters adsorbed on metal oxide (MgO(100)) films of various thicknesses and stoichiometries (that is with and without oxygen vacancies) supported on Mo(100). The Mo(100) single crystal was cleaned and a film of MgO was grown on by evaporating Mg metal in a background of O<sub>2</sub> at a pressure of  $5 \times 10^{-7}$  mbar for a specified time interval. The growth time was calibrated by a break-point analysis and independently by estimating the Mg flux required to achieve a desired thickness. Rather accurate control of film thickness can be achieved through variation of the growth time. The cleanliness and composition of the films and underlying crystal were assessed through the use of Auger electron spectroscopy, and further characterization of the electronic structure of the films was achieved through metastable impact electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS) (see supplementary information).

MIES is a most surface sensitive technique where the de-excitation of the metastable He\* atoms impinging on the surface, takes place 3-10 Å above the surface. For oxide materials the MIES spectra gives direct information about the electronic density of states at the surface. The obtained information is similar to that obtained by UPS, where the kinetic energy and intensity (flux) of electrons ejected from the target material by incident radiation is measured; in the UPS signal, however, contribution of bulk electronic states overlap with those coming from the surface region. In addition to information obtained from UPS spectra about the electronic density of states, the width of

the UPS spectra yields a good estimate of the work functions of the material being studied.

For all the defect-poor films investigated in this work, no contributions in the MIES spectra at binding energies between 1 eV and 3 eV were observed. This is indicative of the absence of F-centers on the thin MgO films.<sup>23</sup> For thin magnesia films, electron states from the underlying Mo surface are visible in the binding energy range of about 9 eV to 11 eV and a decrease of the work function from 3.8 eV (10 ML) to 1.7 eV (1 ML) is observed. The number of F-centre defects can be varied through variation of the Mg evaporation rate, with shorter evaporation times (i.e. faster evaporation) being associated with films with more defects. Such defect-rich substrates were created by us only for films with larger thicknesses (~10 ML); as aforementioned, the presence of these defects was identified by a MIES signal peaked at ~2 eV (see supplementary information).<sup>23</sup>

Clusters of Au<sub>20</sub> were created through the use of a laser ablation source<sup>24</sup> using the 2<sup>nd</sup> harmonic of a 120 Hz Nd:YAG laser. A home-built piezo valve produced a cluster beam from the laser-induced metal plasma using a He carrier gas. The clusters are charge separated with a quadrupole deflector and subsequently mass selected using a quadrupole mass spectrometer (ABB-Extrel; mass limit 4000 amu). The clusters were then soft-landed (with an impingement translational energy of 1 eV/cluster) onto the MgO support up to a coverage of 0.3 % ML (1 ML =  $2.25 \times 10^{15}$  clusters cm<sup>-2</sup>) for temperature programmed reaction (TPR) studies and 0.5 % ML for Fourier transform infrared (FTIR) measurements.

Following the preparation of the Au<sub>20</sub> nanocatalysts TPR and FTIR studies were performed. For the TPR measurements <sup>13</sup>CO and O<sub>2</sub> were dosed onto the surface (at ~100

K) to an exact coverage using a calibrated molecular beam doser. Exposures of one Langmuir (1L) O<sub>2</sub> and 1L <sup>13</sup>CO were administered sequentially. Isotope labeled CO was used to improve the signal-to-noise ratio in the measurements. A temperature programmed ramp of the catalyst was performed between ~100 K and 800 K using a feedback-controlled resistive annealing system of home-built design. Products from the reaction were measured using a quadrupole mass spectrometer. TPR experiments are particularly well suited for the discussion of possible reaction mechanisms as reaction temperatures can be correlated with activation (transition state) energies obtained from first-principles simulations of the reaction mechanism. These combined experimental and theoretical studies give most valuable information about the reaction mechanism, atomic and molecular arrangements, vibrational frequencies, and electronic structure. Such one cycle experiments do not give information about catalytic turn-over frequencies (TOF). Determination of TOF for the catalytic reaction under investigation require added experiments; indeed in certain cases we have applied pulsed molecular beam scattering measurements for this purpose <sup>25, 26</sup>; however, in this paper we do not employ such experiments, focusing on the reaction mechanisms and related atomic and electronic structure factors. Finally we note that a similar dosing procedure was also carried out for FTIR studies. Following the coadsorption of O<sub>2</sub> and <sup>13</sup>CO FTIR measurements were made at a grazing angle of incidence and the stretching frequencies of the <sup>13</sup>CO were determined.

*(b) Theoretical methods.* The first-principles calculations are based on a density functional theory (DFT) approach. <sup>27, 28</sup> We employed the generalized gradient

approximation (GGA) <sup>29</sup> and ultrasoft pseudopotentials <sup>30</sup> (scalar relativistic ones for gold) with a plane wave basis (kinetic energy cutoff of 300 eV). We remark here that such calculations have been shown to give very accurate bond length (up to 1% too long), and reaction barriers that are accurate to within 25%-30% (usually too low) (see page 87 of ref <sup>10</sup>). In structural relaxations corresponding to minimization of the total energy, convergence is achieved when the forces on the atoms are less than 0.001 eV/ Å. In the following we describe certain pertinent details of the calculations.

(i) In the calculations for a 1-layer thick MgO film on Mo(100), a (6 x 6) MgO layer containing 36 atoms of Mg and an equal number of oxygen atoms were used, and the underling Mo(100) substrate was modeled by 4 layers (with a lattice constant of 3.151 Å), each containing 36 Mo atoms. The two bottom layers of the Mo(100) substrate are held static (in the bulk lattice geometry), and in structural optimizations all the other atoms of the system (surface atoms, as well as adsorbed cluster and reactant atoms) are allowed to undergo unconstrained relaxation; note that the MgO lattice was stretched in the surface plane by 5% to accommodate the mismatch between the Mo and MgO lattices.

(ii) In calculations involving an 8-layer thick MgO film on Mo(100), a 5x5 periodic cell, containing 25 atoms per layer was used. In calculations involving a thick MgO crystal (without a metal support) we used six (6 X 6) MgO layers with one or two oxygen vacancies (F-centers) in the top layer; the bottom MgO layer of the slab was kept static with the lattice constant taken as the bulk equilibrium value, 2.998 Å. (all other layers, as well as the adsorbed gold nanocluster and the reactants, were allowed to relax dynamically).



Finally we note that the large size of the computational supercell used by us [up to  $(6 \times 6)$  larger than the planar unit cell of the  $\text{MgO}(100)$  and  $\text{Mo}(100)$  substrate, i.e., equivalent to a  $6 \times 6$   $k$  - point sampling when a single planar unit cell is used for the substrate] justifies the  $k = 0$  ( $\Gamma$  - point sampling) calculations that we employed here. Comparisons between the  $k = 0$  calculations and test computations that included explicit  $k$  - point sampling ( $2 \times 2 \times 1$  and  $4 \times 4 \times 1$ , i.e., increasing the effective number of  $k$  points up to  $24 \times 24 \times 1$ ) provided clear evidence that the  $k = 0$  results are indeed well converged, with differences in total energies well below 1%, and differences (in comparison with the  $k = 0$  results) of at most 1% between the binding energies. We conclude that added  $k$  - point sampling has no discernible effect on the results of our computations.

## **Results and discussion**

### *(a) Experimental findings.*

The isotopically labeled product signals of the temperature-programmed-reaction (TPR) experiments are shown in Fig. 1, where the variation of reactivity with  $\text{MgO}$  film thickness is illustrated for films containing no F-centre defects (labeled as defect-poor films). In a first experiment  $\text{Au}_{20}$  clusters were deposited on a  $\text{Mo}$  support, which was exposed to oxygen at the same conditions as in a typical  $\text{MgO}$  film preparation step ( $5 \times 10^{-7}$  mbar  $\text{O}_2$ ,  $T=300$  K, 20 minutes). The electronic structure of this surface was characterized by MIES and UPS and indicates the presence of a partially oxidized  $\text{Mo}$  surface (see supplementary information). This experiment is rather important since thin  $\text{MgO}$  films of thicknesses of up to about 3 ML are not necessarily continuous, and

consequently  $\text{Au}_{20}$  clusters deposited between MgO islands could be assumed (erroneously as we discuss below) to contribute to the formation of  $\text{CO}_2$  in addition to the reaction catalyzed by the gold clusters anchored on the MgO film. That the inter-island (oxidized Mo) surface regions do not contribute to the CO oxidation reaction has been verified by TPR measurements on  $\text{Au}_{20}$  deposited on partially oxidized Mo surfaces, where no  $^{13}\text{CO}_2$  signal (the product of the oxidation reaction) has been recorded. However, when MgO films grown on the Mo(100) surface are used as supports for the gold clusters, the oxidation reaction is found to occur regardless for various MgO coverages, corresponding to different film thicknesses (Fig. 1(b-d)). In these experiments the MgO film is grown so that the coverage is 3 ML or less. However, as indicated above, it is not assumed that at a film thickness of 1-3 ML the film is continuous; in fact, MgO films on molybdenum are known to grow *via* island formation. It is therefore likely that, although a film is calculated to have 1-3 ML coverage, the film actually consists of islands which are 1 to 3 layers thick, interspaced by partially oxidized Mo. Since, as aforementioned, gold clusters deposited on partially oxidized Mo are not reactive, we conclude that only  $\text{Au}_{20}$  clusters on MgO islands contribute to the observed catalytic activity.

On relatively thin MgO films ( $< 3$  ML) the observed TPR shows two regimes of  $\text{CO}_2$  formation: a minor peak at  $\sim 180$  K with the major product formation occurring at  $\sim 300$  K. The reactivity associated with the nanocatalyst varies as the film thickness is increased. From TPR studies made on thick MgO films ( $\sim 10$  ML), which are found from break-point analysis to be continuous, we observe that the reactivity of the gold catalyst on such films is notably different compared to the thinner MgO film case. In particular,

the TPR records for the thicker films exhibit a single peak at  $\sim 250$  K, which is markedly lower than the higher temperature peak for the aforementioned thin-film-based nanocatalysts.

To explore the effects of film composition on the reactivity, measurements were performed on defect-rich and defect-poor thick films (Fig. 2). Unlike the low temperature reactivity of the defect-poor thick films (Fig. 2(a)) which exhibits a single reaction channel, TPR studies on defect-rich films (Fig. 2(c)) show two reaction regimes. The lower temperature reactivity is observed at  $\sim 200$  K and the higher temperature reactive regime is located in the vicinity of 400 K.

Further investigations of the effects of defects on the  $\text{Au}_{20}$  catalytic activity employed FTIR spectroscopy. Low temperature stretching frequencies of  $^{13}\text{CO}$  coadsorbed with  $^{18}\text{O}_2$  are shown in Fig. 2(b) and 2(d). At low temperature (100 K) and prior to CO-combustion  $\text{Au}_{20}$  on both defect-poor and defect-rich MgO films readily adsorbs  $^{13}\text{CO}$ . Three bands at  $2048\text{ cm}^{-1}$ ,  $2080\text{ cm}^{-1}$ , and  $2130\text{ cm}^{-1}$  are observed for the model catalysts with defect-poor support materials. Note that  $^{13}\text{CO}$  on MgO reveals a typical band at  $2127\text{ cm}^{-1}$  but with less intensity than is observed in the spectrum shown in Fig. 2(b). On defect-rich support materials  $\text{Au}_{20}$  adsorbs  $^{13}\text{CO}$  with vibrational frequencies at  $2063\text{ cm}^{-1}$ ,  $2095\text{ cm}^{-1}$  (observed as small shoulder), and  $2144\text{ cm}^{-1}$ . After initiating the reaction at temperatures larger than 160 K, CO desorbs almost totally, or reacts to completion on  $\text{Au}_{20}$  supported on defect-poor films, whereas for  $\text{Au}_{20}$  supported on defect-rich films CO remains adsorbed at these temperatures. This observation is in concert with the low-temperature catalysis of the CO oxidation reaction, observed for  $\text{Au}_{20}$  clusters supported on defect-poor films. Interestingly, the shift of the main band

observed for CO adsorbed on Au<sub>20</sub> on defect-poor and defect-rich films is only 15 cm<sup>-1</sup> in comparison to 53 cm<sup>-1</sup> in the case of Au<sub>8</sub> adsorbed on identical films.<sup>14</sup>

*(b) Cluster structures, electron charge distribution, and binding energies.*

To elucidate the microscopic mechanisms that underlie the above observations pertaining to the catalytic activity of surface-supported Au<sub>20</sub> clusters, we have performed first-principles density-functional theory (DFT) electronic structure calculations, coupled with atomic structural optimizations and simulations of the reaction pathways, for Au<sub>20</sub> adsorbed on MgO surfaces. While for the thicker MgO films the tetrahedral [i.e. Au<sub>20</sub>(T)] structure of the cluster is by far the most stable one, on thin MgO films supported on Mo(100) a “wetting” planar (quasi two-dimensional, 2D) island configuration (Au<sub>20</sub>(P)) is energetically favorable because of an increased number of contacts with the substrate, leading to a larger accumulation of interfacial charge (originating from the underlying Mo substrate); as noted previously<sup>3</sup> the attraction between the interfacial excess electronic charge and its image in the underlying material substrate is the source of the stabilization of the planar geometry of the deposited gold cluster. However, since in the gas-phase the deposited Au<sub>20</sub> clusters have a tetrahedral 3D structure, it is likely that not all the clusters on the thin MgO(100)/Mo film have attained the optimal 2D structure after deposition. Consequently, for the thin MgO films we consider reactions catalyzed by either the 2D Au<sub>20</sub>(P) adsorbed cluster (Fig. 3(a)), or by the 3D Au<sub>20</sub>(T) isomer (Fig. 3(b)), which are likely to coexist on the surface. Similarly, for the case of a thick MgO(100) crystal containing oxygen vacancies (for TPR experiments see Fig. 2(c)), we consider two possible isomers of the Au<sub>20</sub> cluster. One of these isomers is the tetrahedral Au<sub>20</sub>(T) adsorbed on top of an oxygen vacancy located near the middle of the base facet



of the tetrahedron in Fig. 3(c). The other isomers that we consider are: (i) a bilayer cluster,  $\text{Au}_{20}(\text{bilayer}; \text{FC})$ , adsorbed on an oxygen vacancy located near the middle of the bottom facet (see Fig. 3(d)), and (ii) a bilayer cluster,  $\text{Au}_{20}(\text{bilayer}; 2\text{FC})$ , adsorbed on top of two neighboring F-centers located near the middle of the bottom facet (see Fig. 3(e)). In all these configurations the oxygen vacancies located under the adsorbed gold nanocluster are stable against annealing (for example by one of the oxygens of the reactant molecule).

The optimal structures of the 2D and 3D isomers together with isosurfaces of the excess electron charge distribution,  $\Delta q$ , which is seen to be accumulated mainly in the interface of the cluster with the  $\text{MgO}(1\text{L})/\text{Mo}(100)$  surface, are shown in Figs. 3(a) and 3(b), respectively. The binding energy of  $\text{Au}_{20}(\text{P})$  (Fig. 3(a)) to the surface is  $E_{\text{B}}=12.50$  eV with  $\Delta q=1.62$  e, while  $\text{Au}_{20}(\text{T})$  (Fig. 3(b)) is anchored less strongly, with  $E_{\text{B}}=5.73$  eV and  $\Delta q=1.06$  e; the relaxed structure of  $\text{Au}_{20}(\text{T})$  adsorbed on an 8-layer thick MgO film supported on  $\text{Mo}(100)$  was found to be similar to that shown in Fig. 3(b), with  $E_{\text{B}}=3.00$  eV and  $\Delta q=0.73$  e.

In Fig. 3(c)-3(e) we show ground and higher energy isomeric structures of  $\text{Au}_{20}$  clusters adsorbed on the (100) surface of a thick MgO crystal (with no metal support) with oxygen vacancies, as described above. The binding energies of the clusters  $\text{Au}_{20}(\text{T})$  in (c) and  $\text{Au}_{20}(\text{bilayer})$  in (d) and (e), are 4.36 eV (for (c)), 4.92 eV (for (d)), and 7.93 eV (for the 2FC case displayed in (e)). In the gas phase the tetrahedral cluster is more stable than the bilayer one by 1.57 eV.

Superimposed on the atomic structures in Fig. 3(c) – 3(e) we display the excess electron densities, which show charge accumulation in the interfacial region between the cluster and the surface; this excess charge originates mainly from the F-center defects in

the MgO surface. In addition we show for the  $\text{Au}_{20}(\text{T})$  cluster adsorbed on the single F-center the electronic charge distribution corresponding to the highest occupied Kohn-Sham orbital (HOKS), which is seen to show maxima about the top (apex) atom of the tetrahedron, as well as at the interfacial region in the vicinity of the F-center (see right frame in Fig. 3(c)); adsorption of an oxygen molecule is likely to occur in those regions where the density of the electrons in the HOKS is higher (see below).

*c) Reaction mechanisms of CO combustion on supported  $\text{Au}_{20}$  clusters*

In this section we explore several reaction mechanisms corresponding to the various model catalyst systems investigated in the TPR experiments (Figs. 1 and 2). The reaction profiles (pathways) that we present were obtained via first-principles quantum calculations (see the Theoretical Methods section above). In these calculations a reaction coordinate was judiciously chosen (for example the distance between two reacting atoms, for example the distance between the C atom of an adsorbed CO molecule and the nearest O atoms of an adsorbed  $\text{O}_2$  molecule) and the total energy of the system was optimized for given values of the reaction coordinate, through unconstrained relaxation of all of the other degrees of freedom of the system (reactant molecules, gold cluster atoms, MgO surface atoms, and those of the underlying Mo substrate). The reaction profiles were obtained via repeating such calculations for various values of the chosen reaction coordinate. These calculations yield results that are the same, or close to those obtained by other methods (e.g., the nudged elastic band and variants thereof [see discussion on pages 89-90 in ref. <sup>10</sup>]).

*(i) Low temperature mechanisms of  $\text{Au}_{20}$  adsorbed on thin MgO films.* We model the thin MgO films used in the measurements (Fig. 2(b-d), with MgO coverage up to 1

ML) by an extended monolayer thin MgO film adsorbed on Mo(100). We have found in previous studies that the reactivity of metal supported MgO films remains similar for film thicknesses of up to three layers.<sup>4</sup> Furthermore, we choose to focus on systematic trends correlated with the thickness of the MgO films, and not to consider adsorption of gold clusters onto MgO islands (e.g., adsorption at island step interfaces with the underlying molybdenum oxide), since Au clusters adsorbed on molybdenum oxide (between the MgO islands) are catalytically non-active; the properties of Au clusters adsorbed on the top facet of such MgO islands are similar to those adsorbed on the extended MgO films.

As depicted in Figs 1(b-d) Au<sub>20</sub> deposited on thin MgO films forms CO<sub>2</sub> at temperatures below 200 K in a one-heating cycle experiment. To model possible reaction mechanisms we consider the reactivity of thin film (1-layer MgO) Au<sub>20</sub>/MgO(1L)/Mo systems. Molecular oxygen adsorbs at the interface between the Au<sub>20</sub>(P) cluster and the MgO surface with a binding energy,  $E_B(\text{O}_2/\text{Au}_{20}(\text{P}))$ , of 3.06 eV, the adsorbed molecule is activated to a peroxo state ( $d(\text{O-O}) = 1.515 \text{ \AA}$ ) via occupation of the antibonding  $2\pi^*$  orbital. Clearly oxygen adsorbs on the location of highest charge accumulation. Through transition-state (TS) simulations (consisting, as described above, of ground-state electronic structure calculations and structural relaxations for adiabatically slow variation of the reaction coordinate, i.e. the O-O bond in this case) we determined a dissociation barrier of 0.34 eV with  $d_{\text{TS}}(\text{O-O}) = 1.95 \text{ \AA}$  (Fig. 4(a)). Relaxation from the TS configuration results in the (rightmost) configuration displayed in Fig. 4(a), with  $d(\text{O-O}) = 3.29 \text{ \AA}$ . The reaction between this dissociated configuration of the adsorbed oxygen molecule and a CO molecule adsorbed on top of a surface Mg atom (with a binding energy of 0.47 eV and  $d(\text{CO}) = 1.14 \text{ \AA}$ ) at a distance  $d(\text{C-O}(1)) = 3.10 \text{ \AA}$  between the C

atom and the closest O atom of the adsorbed oxygen molecule (denoted, here and in the following, as O(1)), is shown in Fig. 4(c). In this reaction formation of an adsorbed CO<sub>2</sub> intermediate (TS configuration in Fig. 4(c), with  $d(\text{C-O}(1)) = 1.80 \text{ \AA}$ ,  $d(\text{C-O}) = 1.17 \text{ \AA}$ ,  $d(\text{O-O}(1)) = 3.285 \text{ \AA}$ ) involves an essentially negligible barrier (0.07 eV), and the adsorption energy of the CO<sub>2</sub> product (from the leftmost configuration in Fig. 4(c)) is  $E_{\text{des}} = 0.27 \text{ eV}$ . The bottleneck for this reaction consists of overcoming the relatively low dissociation barrier, and thus this reaction channel contributes to the observed low-T reactivity on the thin MgO film (Fig. 1(b-d)).

Other reaction channels that may contribute to the low-T reactivity are shown in Figs. 4(b) and 4(d), with both involving 3D Au<sub>20</sub>(T)/MgO(1L)/Mo model catalysts. The reaction in Fig. 4(b) again involves dissociative adsorption of O<sub>2</sub> at the interfacial cluster periphery (with a TS barrier of 0.30 eV and  $d_{\text{TS}}(\text{O-O}) = 1.85 \text{ \AA}$ ). Relaxation from the TS configuration results in the (rightmost) structure shown in Fig. 4(b), with  $d(\text{O-O}) = 3.33 \text{ \AA}$ . The reaction of the O(1) atom of the dissociated O<sub>2</sub> molecule with a CO molecule adsorbed with a binding energy of 0.55 eV on the MgO surface is essentially barrierless. Relaxation of the TS complex yields an adsorbed CO<sub>2</sub> intermediate (see inset in Fig. 4(b), with  $d(\text{C-O}(1)) = 1.52 \text{ \AA}$ ,  $d(\text{C-O}) = 1.20 \text{ \AA}$ ,  $d(\text{O-O}(1)) = 3.41 \text{ \AA}$ , whose desorption energy is  $E_{\text{des}} = 0.31 \text{ eV}$ . The other low-T channel, shown in Fig. 4(d), does not involve dissociation of the adsorbed O<sub>2</sub> molecule. Instead it starts from an interfacial-periphery adsorbed O<sub>2</sub> molecule that is activated to a peroxo state ( $d(\text{O-O}) = 1.504 \text{ \AA}$ ), and a CO molecule adsorbed on the MgO surface with a binding energy of 0.41 eV. Formation of CO<sub>2</sub> entails a TS barrier of 0.3 eV (occurring at  $d_{\text{TS}}(\text{C-O}(1)) = 1.58 \text{ \AA}$ ,  $d_{\text{TS}}(\text{O-O}) = 1.54 \text{ \AA}$ ), with subsequent relaxation yielding an adsorbed CO<sub>2</sub> intermediate ( $d(\text{C-O}(1)) = 1.30$



Å,  $d(\text{C-O}) = 1.23$  Å) and an essentially dissociated oxygen molecule ( $d(\text{O-O}(1)) = 3.03$  Å); the desorption energy to form gaseous  $\text{CO}_2$  is 0.16 eV. We note that here, as well as in the other low-T reaction channels discussed above, that diffusion of the reactant CO on the MgO film to the proximity of the adsorbed cluster is assumed<sup>31, 32</sup>.

(ii) *High temperature mechanisms on  $\text{Au}_{20}$  adsorbed on thin MgO films.* The main contribution of the  $\text{CO}_2$  signal in the TPR experiments (Figs 1(b-d)) is observed at around 300 K. While, as described above, for the 2D  $\text{Au}_{20}(\text{P})/\text{MgO}(1\text{L})/\text{Mo}$  catalyst reaction of adsorbed CO with predissociated peripherally adsorbed  $\text{O}_2$  leads to a low-T reaction, when the surface adsorbed CO reacts with an activated, but undissociated peripherally adsorbed  $\text{O}_2$ , a relatively high TS reaction barrier of 0.66 eV is found (Fig. 5(a)), with ( $d_{\text{TS}}(\text{C-O}(1)) = 1.54$  Å,  $d_{\text{TS}}(\text{C-O}) = 1.20$  Å). Subsequent desorption of the adsorbed  $\text{CO}_2$  intermediate involves a desorption energy  $E_{\text{des}} = 0.29$  eV. We note that for this case we considered initial surface adsorption of 2 CO molecules proximal to the gold cluster (with a binding energy of 0.44 eV per molecule, see Fig. 5 (a)). Formation of a second adsorbed  $\text{CO}_2$  molecule via reaction of the second CO with the remaining O atom adsorbed at the gold cluster periphery was found to occur with essentially no activation barrier, but the formation of gaseous  $\text{CO}_2$  entails a relatively high desorption energy  $E_{\text{des}} = 0.60$  eV; note that one of the oxygens of the adsorbed  $\text{CO}_2$  molecule is bonded also to a Mg atom of the magnesia surface, which accounts for the somewhat elevated desorption energy of the product molecule. We conclude that the reactions of both the oxygen atoms with surface adsorbed CO are predicted to contribute to the higher temperature channel observed experimentally.

Another reaction channel that involves a relatively high activation barrier was found for the system CO/O<sub>2</sub>/Au<sub>20</sub>(T)/MgO(1L)/Mo (see Fig.5(b)), where an oxygen molecule is bound to the periphery of the cluster (where the excess charge accumulation is highest) with a binding energy, E<sub>B</sub>(O<sub>2</sub>) of 4.19 eV. The O<sub>2</sub> molecule is peroxo activated (d(O-O) = 1.50 Å) and interacts with an adsorbed CO bonded to the second layer of the 3D gold cluster with E<sub>B</sub> of 0.6 eV. Note that also at this location a slight charge accumulation is calculated (see Fig. 3(b)). The TS barrier is 0.58 eV and the corresponding transition state depicted in Fig. 5(b) is characterized by a d<sub>TS</sub>(C-O(1)) of 2.01 Å, a d<sub>TS</sub>(C-O) of 1.18 Å, and a d(O-O(1)) of 1.47 Å. An upper bound estimate of the desorption energy required for formation of a gaseous CO<sub>2</sub> product is E<sub>des</sub> = 1.06 eV; this rather high calculated desorption energy is attributed to strong bonding of one of the oxygen atoms of the adsorbed product CO<sub>2</sub> molecule to the magnesia surface, with the formation of bonds to two Mg sites of the monolayer MgO film (see Fig. 5(c)), enhanced by the excess accumulation of electronic charge originating from the underlying metal (Mo(100)) support.

(iii) *Reaction mechanisms of Au<sub>20</sub> adsorbed on thick, defect-free MgO films.* To explore the mechanisms underlying the relatively low-temperature reactivity peak at T ≈ 250 K, observed on defect poor thicker (8 - 10 ML) films (Fig 2(a)), we considered a defectless 8-layer thick MgO film, i.e. the model catalyst Au<sub>20</sub>(T)/MgO(8L)/Mo (see Fig. 5(d)). We start from an equilibrated configuration of peripherally adsorbed O<sub>2</sub> (E<sub>B</sub>(O<sub>2</sub>)=0.65 eV in a peroxo-activated state, d(O-O) = 1.41 Å) and a CO molecule bonded (E<sub>B</sub> (CO) = 0.50 eV) to a gold atom in the second layer of the gold cluster. Formation of a TS (Fig. 5(d)) occurs with a low barrier of 0.14 eV at d(C-(O(1))) of 2.0 Å,

and the desorption of  $\text{CO}_2$  involves a very small exit barrier. Note the drastic decrease in the reaction and exit barriers when compared to  $\text{Au}_{20}(\text{T})/\text{MgO}(1\text{ML})\text{Mo}$  (see Fig.5(b)), that is from  $\Delta E_{\text{TS}}=0.58$  eV and  $E_{\text{des}}=1.06$  eV for the thin MgO film, to  $\Delta E_{\text{TS}}=0.14$  eV and to  $E_{\text{des}}=0$  for the thicker one. This illustrates the marked influence of the underlying metal surface on the catalytic activity the adsorbed  $\text{Au}_{20}(\text{T})$  cluster. In particular, the thin MgO layer allows for enhanced charge accumulation (originating from the underlying Mo(100) substrate) which serves to enhance the activation of adsorbed species (specifically  $\text{O}_2$ ). However, the electronic charge transferred through the thin metal-oxide film enhances binding of intermediates and reaction products to the surface, and consequently, in certain cases, one finds for this system higher activation barriers for exit channels corresponding to dissociation of (TS and post-TS) intermediate reaction complexes, or desorption of the product molecule (e.g.  $\text{CO}_2$ ).

(iv) *Reaction mechanisms on  $\text{Au}_{20}$  on defective thick MgO films.* In all the cases discussed above the MgO films were defectless, and the catalytic activity was enabled by the excess electronic charge (originating from the underlying metal (Mo(100)) support) accumulated at the interface of the gold nanocluster with the magnesia film. We turn now to analysis of the experiments performed on a defect rich thick MgO(100) surface, where any effects due to an underlying metal support are absent. In the data shown for this system in Fig. 2(c), the broad distribution of the reactivity (the smaller peak at  $\sim 210$  K and the main broad distribution peaking at  $\sim 400$  K) can be correlated with the multiplicity of adsorbed cluster configurations that may coexist on such surfaces. These competing configurations differ from each other by the isomeric structure of the adsorbed nanocluster and the nature of the binding of the cluster to the surface; in particular, we

consider anchoring of clusters to single or double (nearest-neighbor) surface oxygen vacancy (F-centre) defects. (see Fig. 3(c-e). First we considered a single FC defect located under the middle of the bottom facet of the adsorbed tetrahedral  $\text{Au}_{20}$  cluster ( $\text{Au}_{20}(\text{T})/\text{MgO}(\text{FC})$ ), whose binding energy to the MgO surface is 4.36 eV. An  $\text{O}_2$  molecule adsorbs to the top apex gold atom of the  $\text{Au}_{20}(\text{T})$  cluster with a binding energy,  $E_{\text{B}}(\text{O}_2) = 0.28$  eV and a bond distance,  $d(\text{O}-\text{O}) = 1.28$  Å (see Fig. 6(a)); we recall here that for this system the HOKS orbital exhibited electronic charge accumulation at the apex atom (see right frame in Fig. 3(c)), where the  $\text{O}_2$  molecule adsorbs. It reacts with adsorbed CO ( $E_{\text{B}}(\text{CO}) = 0.54$  eV), reaching a relatively low TS barrier of 0.41 eV at  $d_{\text{TS}}(\text{C}-\text{O}(1)) = 1.75$  Å,  $d_{\text{TS}}(\text{C}-\text{O}) = 1.18$  Å, and  $d_{\text{TS}}(\text{O}-\text{O}(1)) = 1.35$  Å (see 6 (a)), and resulting in a post TS CO- $\text{O}_2$  complex (see leftmost configuration in Fig. 6(a)). Dissociation of the complex requires an energy  $E_{\text{diss}} = 0.49$  eV and desorption of the product  $\text{CO}_2$  molecule occurs with no exit barrier.

Other initial adsorption configurations that we have explored include peripherally adsorbed  $\text{O}_2$  with CO adsorbed either on the MgO surface or on the tetrahedral cluster. In all these cases we obtained activation barriers in the range of 0.6 to 0.75 eV. For example starting from a peripheral adsorption of  $\text{O}_2$  ( $E_{\text{B}}(\text{O}_2) = 0.64$  eV) yielding a peroxo activated molecule ( $d(\text{O}-\text{O})=1.49$  Å) and a CO molecule adsorbed on the MgO surface ( $E_{\text{B}}(\text{CO})=0.28$  eV,  $d(\text{C}-\text{O}(1))=3.02$  Å,  $d(\text{C}-\text{O})=1.14$  Å), resulted in a transition state barrier  $\Delta E_{\text{TS}} = 0.62$  eV, with  $d_{\text{TS}}(\text{C}-\text{O}(1))= 1.65$  Å,  $d_{\text{TS}}(\text{C}-\text{O})=1.18$  Å and  $d_{\text{TS}}(\text{O}-\text{O})=1.56$  Å, which relaxes to a state with an adsorbed  $\text{CO}_2$  molecule ( $d(\text{C}-\text{O}(1))=1.18$  Å,  $d(\text{C}-\text{O})=1.17$  Å, and  $d(\text{O}-\text{O}) = 3.20$  Å). Desorption of the product  $\text{CO}_2$  molecule is found to involve a negligible barrier. .



Next we consider several reaction pathways involving a bilayer isomeric form of the adsorbed  $\text{Au}_{20}$  cluster (see Fig. 3(d and e)):

(A) First we display in Fig. 6(b) the pathway for the reaction on a bilayer isomer anchored on a single FC defect (the binding energy of the cluster to the surface is calculated to be 4.92 eV). Here the reaction starts from a peripherally adsorbed  $\text{O}_2$  molecule ( $E_B(\text{O}_2) = 0.63$  eV) which is activated to a peroxo state ( $d(\text{O}-\text{O}) = 1.43$  Å), and a surface adsorbed CO molecule ( $E_B(\text{CO}) = 0.29$  eV) with the distance between the carbon atom to the nearest oxygen of the  $\text{O}_2$  molecule  $d(\text{C} - \text{O}(1)) = 2.48$  Å. The transition state barrier for the formation of an adsorbed CO- $\text{O}_2$  complex (characterized by  $d_{\text{TS}}(\text{C}-\text{O}(1)) = 1.60$  Å,  $d_{\text{TS}}(\text{C}-\text{O}) = 1.20$  Å and , and  $d_{\text{TS}}(\text{O}-\text{O}(1)) = 1.49$  Å) is 0.29 eV, and dissociation of the interoxygen bond between the complex and the other oxygen of the reactant  $\text{O}_2$  molecule entails an activation energy  $E_{\text{diss}}(\text{O}-\text{O}) = 0.43$  eV. Desorption of the product  $\text{CO}_2$  molecule from the surface is barrierless.

(B) A somewhat higher temperature reaction pathway is shown in Fig. 6(c) for a reaction catalyzed by a bilayer cluster adsorbed on top of two neighboring oxygen vacancies, both located in the vicinity of the middle of the bottom facet of the cluster. The binding energy of this isomer to the surface is  $E_B(\text{Au}_{20}(\text{bilayer})) = 7.93$  eV (see Fig. 3(e)). The reaction starts from a peripherally adsorbed ( $E_B(\text{O}_2) = 0.84$  eV) peroxo activated ( $d(\text{O}-\text{O}) = 1.51$  Å) oxygen molecule, and a CO molecule adsorbed on the bilayer gold cluster ( $E_B(\text{CO}) = 0.81$  eV). The barrier for formation of a TS CO- $\text{O}_2$  complex is 0.26 eV, and the dissociation process of the complex (see above) entails an energy  $E_{\text{diss}} = 0.51$  eV. Desorption of the product  $\text{CO}_2$  molecule is found to be barrierless.

We digress here to illustrate one of the key principles of nanocatalysis – namely “dynamical structural fluctuationality”<sup>18</sup> – which expresses the ability of the catalytic centre (here the surface-supported gold nanocluster) to change its atomic structure (atomic arrangement) in the course of the reaction. This property is illustrated by following, in the course of the oxidation reaction, the relative positions of the three gold atoms marked (by numbers 1, 2, and 3) in the inset to Fig. 6(c). In the initial state (minimum energy configuration) of the adsorbed reactants (rightmost structure in Fig. 6(c)) the angle formed by the three marked Au atoms (with the atom marked 2 being at the apex of the triangle), takes the value  $\theta(123) = 59^\circ$ . As the transition state is approached (decreasing the distance  $d(\text{C-O}(1))$  between the C atom and the closest oxygen atom of the adsorbed  $\text{O}_2$  molecule) the above angle increases to a value of  $\theta_{\text{TS}}(123) = 76^\circ$ . The relaxed configuration (leftmost structure in Fig. 6(c)) is characterized by  $\theta(123) = 79^\circ$ . We note here, that the fluxional structural distortions of the metal cluster, illustrated above, occur to various degrees in all the reactions described in this study, with the largest structural distortions observed when both reactants adsorb on the metal cluster. These structural variations serve to enhance the adsorption of the reactants, and to lower the activation barriers for reactions between the adsorbed reactants. We note here that the activation of the reactant  $\text{O}_2$  molecule (to form a superoxo or a peroxo like state through occupation of the antibonding orbital, as discussed above), which is manifested by elongation of the O-O bond of the adsorbed molecule (located often at the cluster peripheral interface with the underlying MgO surface) by up to  $\Delta d(\text{O-O}) = 0.25 \text{ \AA}$ , is accompanied by changes in the positions (relative distances) of the gold atoms in the vicinity of the adsorption site.

(C) As an example of a higher-temperature reaction we show in Fig. 6(d) the pathway of a reaction catalyzed by the bilayer gold cluster adsorbed on a single surface FC (as in Fig. 6(b)), starting from a peripherally adsorbed, and peroxo activated,  $O_2$  molecule ( $E_B(O_2) = 0.96$  eV,  $d(O-O) = 1.50$  Å) and a surface adsorbed CO molecule ( $E_B(CO) = 0.27$  eV) located at a distance  $d(C-O(1)) = 3.14$  Å between the C atom and the nearest oxygen of the adsorbed  $O_2$  molecule. This reaction involves a TS energy barrier of 0.68 eV, and breakup of the transition state complex resulting in desorption of the product  $CO_2$  molecule occurs with no barrier.

The above examples, drawn from an ensemble of configurations corresponding to calculated reaction profiles with activation barriers in the range of about 0.35 eV to 0.75 eV, correlate well with the observed broad temperature distribution measured for the CO reaction on  $Au_{20}$  clusters deposited on thick defect-rich MgO surfaces (Fig. 2(c)).

## Summary

The oxidation of CO on  $Au_{20}$  sensitively depends on the thickness of the MgO film grown on a Mo(100) single crystal as well as on the metal-oxide stoichiometry that is surface defect density. These dependencies are reflected in variations of the reaction temperatures observed in temperature programmed desorption single-heating-cycle experiments, as well as in the amount of produced  $CO_2$ . The first-principles theoretical investigations presented here show that the observed changes in reactivity may be correlated, in part, with a dimensionality cross-over from 3D tetrahedral  $Au_{20}$  in the case of thick films ( $\geq 8$  ML) to 2D “wetting” planar structures for film thicknesses of less than  $\sim 3$  ML; we note here that we have shown (see also the Supplemental Information)

through MEIS and UPS measurements that these thin MgO films are highly stoichiometric, that is they may contain only a very low number density of (Lewis-base type) oxygen-vacancy (F-center) defects.

Underlying the aforementioned structural and dimensionality variations is the enhanced charge transfer from the underlying Mo surface through the metal-oxide occurring for the thinner films. This transferred charge accumulates mainly at the interfacial region of the adsorbed metal cluster with the metal-oxide, and it stabilized planar (wetting) configurations of the cluster (through attractive image charge interactions, which increase with the contact area of the metal cluster with the surface.<sup>3</sup>,<sup>4</sup> Furthermore, the excess charge, can enhance the chemical catalytic activity of the adsorbed (partially charged) gold clusters (both 3D and 2D), via transfer of charge to adsorbed reactant molecules<sup>4</sup>; for example activation of adsorbed O<sub>2</sub> through population of the 2 $\pi^*$  antibonding orbital and formation of a superoxo or peroxo activated molecule, which may react with CO in a Langmuir – Hinshelwood mechanism entailing a lower activation barrier. On the other hand, the excess interfacial charge accumulation for thin metal-oxide films may enhance the binding strength of reaction intermediates and/or adsorbed product molecules, thus causing larger exit reaction barriers. Such reaction mechanisms have been illustrated in this study for both 2D and 3D Au<sub>20</sub> nanoclusters adsorbed on thin MgO(1L)/Mo(100).

For thick films and 3D Au<sub>20</sub> adsorbed clusters (both tetrahedral and bilayer isomeric structures) charge accumulation, with the concomitant charging of the adsorbed clusters, can be induced by defect sites of Lewis base character (e.g. oxygen vacancies, F-centers). This charge accumulation is local and it depends on the type of the electron



donor. In both cases, charging through thin metal-oxide films and F-center-induced charging, the excess charge is found to be located mainly on the perimeter atoms of the 2D or 3D adsorbed  $\text{Au}_{20}$  clusters; we also find that in the case of a 3D tetrahedral  $\text{Au}_{20}(\text{T})$  cluster anchored to a MgO surface F-center, the highest occupied Kohn-Sham orbital exhibits an enhanced electronic density localized on the top apex atom of the tetrahedron. The charge accumulation defines the location of the reactive site on the cluster and thus reactivity can be tuned as a function of the properties (thickness and stoichiometry) of the supporting metal-oxide film.

We believe that the concepts and methodologies developed in this paper, and the demonstrated ability to control and tune the catalytic reactivity of gold nanoclusters through variations of the thickness and/or composition of the support (here MgO(100) grown on the surface of Mo(100)), are of importance for the development of effective gold-based nanocatalytic systems. Moreover, it will be of great interest to explore the extension of these concepts and control methods to nanocatalytic systems based on other combinations of metal nanoclusters and oxide supports.

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## Figure Captions

Fig 1: Temperature programmed reaction (TPR) spectra illustrating the  $^{13}\text{CO}_2$  formation produced using a nanocatalyst based on  $\text{Au}_{20}$  clusters at a coverage of 0.3 %ML deposited onto MgO films of various thickness (1-10 ML). Markers represent the experimental data points, the solid line is a multipeak exponential Gaussian fit of data to guide the eye.

Fig 2: (a) TPR measurements made on  $\text{Au}_{20}$  based nanocatalysts using thick, defect-poor MgO films ( $\sim 10$  ML). Markers show the experimental data points and the line is a multipeak exponential Gaussian fit of the data. (c) TPR measurements made on  $\text{Au}_{20}$  based nanocatalysts using thick, defect-rich MgO films. Markers show the experimental data points and the line is a multipeak exponential Gaussian fit of the data. Figures (b) and (d) are FTIR studies corresponding to figures (a) and (c), respectively. All measurements are made with a 0.5 %ML coverage of  $\text{Au}_{20}$ .

Fig. 3: Minimum energy structures of  $\text{Au}_{20}$  clusters adsorbed on surfaces. (a) top (left) and side (right) views of a planar gold cluster adsorbed on a 1-layer thick MgO layer, supported on Mo(100),  $\text{Au}_{20}(\text{P})/\text{MgO}(1\text{L})/\text{Mo}$ . (b) same as in (a) for a 3D tetrahedral gold cluster. The binding energies of the clusters (with reference to the separated gas-phase clusters and surface subsystems) are: 12.50 eV for the planar cluster (a) and 5.73 eV for the 3D one (b). Superimposed on the atomic structures are density isosurfaces corresponding to the excess electronic charge distributions (blue corresponds to charge

accumulation and pink signifies charge depletion with reference to the isolated cluster and surface components); these excess electron distributions are obtained from the difference between the charge distribution of the combined system (i.e. gold cluster adsorbed on the MgO surface ,with or without a Mo(100) support) and the charge distributions of the isolated components (in the optimal geometry determined for the combined system), that is: (i) the Au<sub>20</sub> gold cluster and (ii) the MgO surface (with or without a Mo(100) support). Note charge accumulation at the interfacial periphery regions. (c) Left: excess electronic charge distribution for a tetrahedral Au<sub>20</sub> cluster adsorbed on an F-centre (on the surface of a thick MgO film), located under the middle of the bottom facet of the cluster; configuration A in the text. Right: Electron density isosurface of the highest occupied Kohn-Sham orbital, showing charge accumulation about the top apex atom, as well as near the oxygen vacancy; the isosurface encompasses 61% of the electron density in the doubly occupied orbital (i.e. 1.23 e). (d) A bilayer isomer of Au<sub>20</sub> with a surface F-centre located near the middle of the bottom facet of the adsorbed cluster. (e) A bilayer cluster with a dimer of neighboring F-centers located near the middle of the bottom fact of the adsorbed cluster. The binding energies of the clusters to the MgO surface (with reference to the energy of the isolated systems, MgO surface, and the corresponding gas-phase cluster, i.e., Au<sub>20</sub>(T) in (c) and Au<sub>20</sub>(bilayer) in (d) and (e), are 4.36 eV (for (c), 4.92 eV (for (d), and 7.93 eV (for the 2 FC case displayed in (e)). In the gas phase the tetrahedral cluster is more stable than the bilayer one by 1.57 eV. Superimposed in (c) and (d) are equi-density surfaces of the excess electron charge density; blue and pink corresponding to charge excess and charge depletion, respectively. Note charge accumulation on the top apex atom of the cluster in (c), and near the edge in



(d) and (e). The excess electronic charges are: (c)  $\Delta q$  ( $\text{Au}_{20}(\text{T}; \text{FC})$ )=1.80 e, (d)  $\Delta q$  ( $\text{Au}_{20}(\text{bilayer}; \text{FC})$ )= 2.10 e for the bi-layer isomer in (d), and (e)  $\Delta q$  ( $\text{Au}_{20}(\text{bilayer}; 2\text{FC})$ )= 2.85 e. Color designation: Au atoms in yellow, oxygen atoms in red, Mg in green, and Mo atoms in black.

FIG. 4 (a) and (b): Reaction paths for the dissociation of  $\text{O}_2$  on 2D and 3D (tetrahedral)  $\text{Au}_{20}$  adsorbed on a one layer thin MgO film supported on Mo(100). In both cases the transition state (TS) activation energy is relatively low:  $\Delta E_{\text{TS}} = 0.34$  eV for the 2D gold structure (a), and  $\Delta E_{\text{TS}} = 0.30$  eV for the 3D adsorbed cluster (b). In the insert to frame (b) we show the relaxed structure of the adsorbed  $\text{CO}_2$  molecule produced by the reaction of the dissociated oxygen molecule on  $\text{Au}_{20}(\text{T})/\text{MgO}(1\text{L})/\text{Mo}$  with CO; no energy barrier is involved in this reaction, which starts from the dissociated oxygen molecule and a CO adsorbed on the MgO surface (on top of an Mg atom, with an adsorption energy of 0.55 eV), at a distance of 2.48 Å between the C atom and the closest dissociated O atom. The desorption energy of the product  $\text{CO}_2$  is 0.31 eV. This reaction contributes to the low-temperature peak shown in Fig. 1. In (c) and (d) we display two other low-temperature reactions pathways. The reaction in (c) corresponds to an adsorbed planar,  $\text{Au}_{20}(\text{P})$  cluster, and it starts from the adsorbed dissociated oxygen molecule shown in (a) (with a dissociation activation energy of 0.34 eV) and a CO molecule adsorbed on top of a Mg atom ( $E_{\text{B}}(\text{CO}) = 0.47$  eV). The generation of adsorbed  $\text{CO}_2$  entails a transition state barrier of  $E_{\text{TS}} = 0.07$  eV and a desorption energy of the product  $E_{\text{des}}(\text{CO}_2) = 0.27$  eV). The reaction in (d) corresponds to an adsorbed 3D  $\text{Au}_{20}(\text{T})$  cluster, and it involves a peripherally adsorbed activated oxygen molecule, and a CO molecule adsorbed on the

MgO surface ( $E_B = 0.41$  eV). The reaction in (d) entails a TS barrier  $\Delta E_{TS} = 0.30$  eV, and the desorption energy of the product is  $E_{des}(\text{CO}_2) = 0.16$  eV. Color designation (online): Mg atoms in green, O atoms in red, Au atoms in yellow, C atoms in light gray, Mo atoms in dark gray.

FIG. 5 (a-c) High temperature pathways of CO with  $\text{O}_2$  catalyzed by for  $\text{Au}_{20}$  adsorbed on 1L MgO/Mo (100). (a) Formation of  $\text{CO}_2$  through the reaction of a CO molecule adsorbed on the MgO surface with  $E_B(\text{CO}) = 0.44$  eV, near an activated oxygen molecule adsorbed at the interfacial periphery of a planar (2D)  $\text{Au}_{20}(\text{P})$  cluster on the 1L MgO film with  $E_B(\text{O}_2) = 3.06$  eV,  $d(\text{O}-\text{O}) = 1.52$  Å. The reaction entails a TS energy barrier of 0.66 eV, and the desorption of the  $\text{CO}_2$  product requires  $E_{des} = 0.29$  eV. The reaction with the second adsorbed CO with the remaining oxygen atom proceeds with no activation barrier, however the desorption of the resulting adsorbed  $\text{CO}_2$  molecule requires an energy of 0.60 eV. (b) Pathway of the oxidation reaction catalyzed by a tetrahedral 3D  $\text{Au}_{20}(\text{T})$  cluster, with an activated  $\text{O}_2$  molecule adsorbed at the peripheral interface of the cluster with the underlying 1L MgO film ( $E_B(\text{O}_2) = 4.19$  eV) and a CO molecule adsorbed on the gold cluster ( $E_B(\text{CO}) = 0.6$  eV). The transition state barrier for the reaction is 0.58 eV, and desorption of the product  $\text{CO}_2$  molecule requires 1.06 eV. (c) An enlarged view of the desorbing  $\text{CO}_2$  molecule, showing a configuration with the carbon bonded to the gold cluster and one of the oxygen atoms bonded to two Mg surface sites ( $d(\text{O}-\text{O}) = 2.08$  Å), resulting in a relatively high desorption energy. (d) The CO combustion reaction pathway catalyzed by a tetrahedral  $\text{Au}_{20}(\text{T})$  cluster adsorbed on an eight-layer-thick MgO film supported on Mo(100), see Fig. 2(a)). In the initial configuration an activated  $\text{O}_2$

molecule is adsorbed ( $E_B(O_2) = 0.65$  eV) at the cluster interface with the magnesia film, and a CO molecule is bonded to a second-layer Au atom of the cluster ( $E_B(CO) = 0.50$  eV). Formation of a  $CO_2$  product entails a 0.14 eV transition state barrier, and the molecule desorbs readily.

Color designation (online): Mg in green, O in red, Au in yellow, C in light gray, Mo in dark gray.

Fig. 6 Reaction pathways for  $Au_{20}$  clusters adsorbed on oxygen vacancies, surface F-centers, on thick  $MgO(100)$  surfaces, corresponding to the experimental data displayed in Fig. 3(c). (a) Reaction profile for a reaction catalyzed by a 3D tetrahedral  $Au_{20}(T)$  cluster adsorbed on a single FC located under the middle of the bottom facet of the cluster, whose binding energy to the  $MgO$  surface is 4.36 eV. An  $O_2$  molecule binds to the top apex gold atom of the  $Au_{20}(T)$  cluster with a binding energy,  $E_B(O_2) = 0.28$  eV, and it reacts with an adsorbed CO ( $E_B(CO) = 0.54$  eV), reaching a relatively low TS barrier of 0.41 eV. Dissociation of the CO- $O_2$  complex requires a dissociation energy  $E_{diss} = 0.49$  eV, and desorption of the  $CO_2$  product is barrierless. (b)-(d): Reaction pathways catalyzed by bilayer  $Au_{20}$  cluster isomers. (b) Pathway for the reaction on a bilayer isomer anchored on a single FC defect. The reaction starts from a peripherally adsorbed, peroxy activated,  $O_2$  molecule ( $E_B(O_2) = 0.63$  eV) and a surface adsorbed CO molecule ( $E_B(CO) = 0.29$  eV). The transition state barrier for the formation of an adsorbed CO- $O_2$  complex is 0.29 eV, and dissociation of the O-O bond between the complex and the other oxygen of the reactant  $O_2$  molecule  $E_{diss}(O-O) = 0.43$  eV. Desorption of the product  $CO_2$  molecule from the surface is barrierless. (c) The CO combustion reaction catalyzed by a

bilayer cluster adsorbed on top of two neighboring oxygen vacancies. The reaction starts from a peripherally adsorbed ( $E_B(\text{O}_2) = 0.84 \text{ eV}$ ) peroxy activated oxygen molecule, and a CO molecule adsorbed ( $E_B(\text{CO}) = 0.81 \text{ eV}$ ) on the bilayer gold cluster. The barrier for formation of a TS CO-O<sub>2</sub> complex is 0.26 eV, and the dissociation process of the complex entails an energy  $E_{\text{diss}} = 0.51 \text{ eV}$ . Desorption of the product CO<sub>2</sub> molecule is found to be barrierless. In the inset gold atoms whose positions markedly distort during the reaction (that is, exhibiting dynamic structural fluctuation) are designated as 1, 2 and 3. The distances between these atoms at various stages of the reaction are as follows: initial (rightmost) configuration:  $d(1-2) = 2.95 \text{ \AA}$ ,  $d(2-3) = 3.35 \text{ \AA}$ ,  $d(1-3) = 3.14 \text{ \AA}$ , and  $\theta(123) = 59^\circ$ ; Transition state configuration:  $d(1-2) = 2.89 \text{ \AA}$ ,  $d(2-3) = 3.11 \text{ \AA}$ ,  $d(1-3) = 3.68 \text{ \AA}$  and  $\theta(123) = 76^\circ$ ; Post-TS configuration (corresponding to  $d(\text{C-O}(1)) = 2.09 \text{ \AA}$ ):  $d(1-2) = 2.94 \text{ \AA}$ ,  $d(2-3) = 3.27 \text{ \AA}$ ,  $d(1-3) = 3.96 \text{ \AA}$ , and  $\theta(123) = 79^\circ$ . (d) Pathway of the reaction catalyzed by the bilayer gold cluster adsorbed on a single surface FC (as in Fig. 6(b)), starting from a peripherally adsorbed, peroxy activated, O<sub>2</sub> molecule ( $E_B(\text{O}_2) = 0.96 \text{ eV}$ ), and a surface adsorbed CO molecule ( $E_B(\text{CO}) = 0.27 \text{ eV}$ ). The reaction involves a TS energy barrier of 0.68 eV, and breakup of the transition state complex resulting in desorption of the product CO<sub>2</sub> molecule occurs with no energy barrier. Color designation (online): Mg in green, O in red, Au in yellow, C in light gray.



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